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## Zeolite-Containing Remedial Compositions

### Cross-Reference to Related Applications

[0001]      This application is a continuation-in-part of prior Application No. 10/686,098 filed October 15, 2003, the entire disclosure of which is incorporated herein by reference, which itself is a continuation-in-part of prior Application No. 10/623,443 filed July 18, 2003, the entire disclosure of which is incorporated herein by reference, and which itself is a continuation-in-part of prior Application No. 10/315,415, filed December 10, 2002, the entire disclosure of which is incorporated herein by reference.

### Background

[0002]      The present embodiments relate generally to wellbore treating fluids introduced into a subterranean zone penetrated by a wellbore, particularly fluids introduced as remedial compositions such as pills.

[0003]      Conventionally, a wellbore is drilled using a drilling fluid that is continuously circulated down a drill pipe, through a drill bit, and upwardly through the wellbore to the surface. Typically, after a wellbore has been drilled to total depth, the drill bit is withdrawn from the wellbore, and circulation of the drilling fluid is stopped, thereby initiating a shut-down period. The drilling fluid is left in the wellbore to provide hydrostatic pressure (i.e., hole stability) on permeable formations penetrated by the well bore, thereby preventing the flow of formation fluids into the wellbore. Another function provided by the drilling fluid left in the wellbore is to prevent lost circulation, by sealing off the walls of the wellbore so that the drilling fluid is not lost into highly permeable subterranean zones penetrated by the wellbore. Sealing off the walls of the wellbore is typically accomplished during the shut down period by the deposit of a filter

cake of solids from the drilling fluid, and additional dehydrated drilling fluid and gelled drilling fluid, on the walls of the wellbore.

**[0004]** The next operation in completing the wellbore usually involves running a pipe string, e.g., casing, into the wellbore. After the pipe is run in the wellbore, the next operation typically involves cleaning out the wellbore, which may be accomplished by re-initiating circulation of drilling fluid. After clean-up operations are performed in the wellbore, primary cementing operations are typically performed therein. Namely, the pipe is cemented in the wellbore by placing a cement slurry in the annulus between the pipe and the walls of the wellbore.

**[0005]** During any of the above or other operations performed in the wellbore, a number of problems can occur that require remedial operations. One such problem is lost circulation. Lost circulation occurs when the drilling fluid is "lost" into the subterranean zone penetrated by the wellbore. The drilling fluid can be lost when the drill bit encounters spaces such as fissures, fractures, or caverns in the subterranean zone, and the drilling fluid flows into such spaces. Lost circulation can also occur when the hydrostatic pressure provided by the drilling fluid in the wellbore is compromised. This occurs when the drill bit encounters other types of "spaces", such as unfavorable subterranean zones, which may be comparatively low pressure subterranean zones, such as vugs, fractures, and other thief zones, and similarly, comparatively high pressure subterranean zones. When lost circulation occurs, remedial steps are required.

**[0006]** Most remedial steps for lost circulation comprise introducing a remedial composition into the wellbore to seal the above-described spaces. Examples of such remedial compositions comprise mixtures of clay and aqueous rubber latex or hydratable polymer (e.g., U.S. Pat. Nos. 5,913,364; 6,060,434; 6,167,967; 6,258,757), which form masses with a consistency often referred to as "rubbery", "viscous", or "gelatinous", to seal the space. Exemplary remedial compositions form such masses upon contact with drilling fluid, mud or other compositions with which the remedial composition is designed to react, thereby sealing fractures, fissures, low pressure or high pressure subterranean zones, and the like. Such remedial compositions are often referred to as a "pill" by those of ordinary skill in the art.

**[0007]** The present embodiments provide compositions in the form of remedial compositions, such as pills, that comprise zeolite, as well as methods for the use of such remedial compositions comprising zeolite.

### **Description**

**[0008]** According to embodiments described herein, wellbore treating fluids comprising zeolite are introduced into a wellbore in the form of a remedial composition such as a pill. In one embodiment, the wellbore treating fluid comprises a pill comprising zeolite.

**[0009]** Methods according to the present embodiments provide for introducing a wellbore treating fluid comprising zeolite into a subterranean zone penetrated by a wellbore to remediate lost circulation, and to seal fissures, fractures, caverns, vugs, thief zones, low pressure or high pressure subterranean zones.

**[0010]** Remedial compositions that generally form a mass upon contact with a drilling fluid, mud or other composition with which the remedial composition is designed to react are referred to herein as a “pill”. As used herein, the term “mud” encompasses any fluid used in hydrocarbon drilling operations, including but not limited to all types of water-base, oil-base and synthetic-base drilling fluids, and fluids that contain significant amounts of suspended solids, emulsified water or oil.

**[0011]** According to the present embodiments, a pill comprising zeolite and at least one carrier fluid is provided. Pills according to the present embodiments can be used with any methods in which conventional remedial compositions are used. For example, a pill according to the present embodiments can be used as a remedial composition for lost circulation. The carrier fluid can be one or more oil-based or water-based fluids as illustrated further herein. The zeolite and carrier fluid (whether water-based or oil-based) are referred to herein as “base components” of the pill to provide a point of reference for additional components such as activators and surfactants. According to one embodiment, the zeolite is present in an amount of from about 5 to about 75 weight percent of the total weight of the base components. According to other embodiments, zeolite is present in an amount of from about 20 to about 60 weight percent of the total weight of the base components. According to still other embodiments, zeolite is present in an amount of from about 30 to about 50 weight percent of the total weight of the base components.

**[0012]** Whether the at least one carrier fluid is water-based or oil-based, embodiments of the pill herein comprise carrier fluid in an amount from about 25 to about 95 weight percent of the total weight of the base components. According to other embodiments, carrier fluid is present in

an amount of from about 40 to about 80 weight percent of the total weight of the base components. According to still other embodiments, carrier fluid is present in an amount of from about 50 to about 70 weight percent of the total weight of the base components.

**[0013]** When the drilling fluid, mud, or other composition with which the pill comprising zeolite is desired to react is water-based, then the pill comprises zeolite and at least one oil-based carrier fluid. Alternatively, the carrier fluid is a synthetic-based fluid. When such oil-based (or synthetic-based) pill is introduced into the wellbore, it will react when it comes into contact with the water-based fluid, thereby forming a mass.

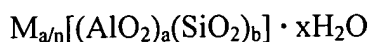
**[0014]** According to another embodiment, when the drilling fluid, mud or other composition with which the pill comprising zeolite is desired to react is oil-based or synthetic-based, then the pill comprises zeolite and at least one water-based carrier fluid. Thus, when such water-based pill is introduced into the wellbore, it will react when it comes into contact with the oil-based or synthetic-based drilling fluid, thereby forming a mass.

**[0015]** According to yet another embodiment, when the pill comprising zeolite is oil-based or synthetic-based, or when the drilling fluid, mud or composition with which the pill is desired to react is oil-based or synthetic-based, the pill further comprises at least one surfactant. Surfactants are known to those of ordinary skill in the art, and the selection of a type and concentration of a surfactant largely depends on the nature and composition of the pill, which can be determined by those of ordinary skill in the art. Suitable surfactants for use with the present embodiments include but are not limited to cetyltrimethylammonium chloride, cocoalkyltrimethylammonium chloride, cocoalkyldimethylbenzyl ammonium chloride, stearyltrimethylammonium chloride, alkylbehenyltrimethylammonium chloride dihydrogenatedtallowalkylethylmethyleammonium ethosulfate, didecyldimethylammonium chloride, dicocyldimethylammonium chloride, distearyldimethylammonium chloride, dioleyldimethylammonium chloride, trilaurylmethylammonium chloride, cocoyl-bis-(2-hydroxyethyl)methylammonium chloride, polyoxyethylene (15) cocoalkylmethylammonium chloride, olyel-bis-(2-hydroxyethyl)methylammonium chloride, tallowalkylmethylpropylenediammonium dichloride, and trimethyltallowammonium chloride. According to one embodiment illustrated herein, a remedial composition comprising zeolite and at least one carrier fluid further comprises trimethyltallowammonium chloride as a surfactant.

**[0016]** According to still other embodiments, an activator is incorporated into the pills of the present embodiments in an amount of from about 1 to about 20 weight percent based on the total weight of the base components of the pill. The activator can be any of calcium hydroxide, sodium silicate, sodium fluoride, sodium silicofluoride, magnesium silicofluoride, zinc silicofluoride, sodium carbonate, potassium carbonate, sodium hydroxide, potassium hydroxide, sodium sulfate, and mixtures thereof. Selection of type and concentration of an activator(s) largely depends on the nature and composition of the pill. Typically, the activator is selected so that it will add strength to the mass formed when the pill is contacted with a drilling fluid, mud, or other composition with which it is designed to react. According to one embodiment, the activator is calcium hydroxide (commonly referred to as lime).

**[0017]** As described above, conventional pills comprise materials that form a mass upon contact with the drilling fluid, mud or other composition with which the pill is designed to react, thereby sealing spaces such as fissures, fractures, caverns, vugs, thief zones, low pressure or high pressure subterranean zones and preventing lost circulation. Pills comprising zeolite according to embodiments presented herein develop compressive strength over time, which results in an enhanced sealing of such spaces. Moreover, the sealing of such spaces according to the present embodiments strengthens the wellbore formation such that higher density muds, drilling fluids, and other wellbore treating fluids can be pumped through the wellbore without compromising the stability of the wellbore.

**[0018]** Zeolites are porous aluminosilicate minerals that may be either a natural or manmade material. Manmade zeolites are based on the same type of structural cell as natural zeolites, and are composed of aluminosilicate hydrates having the same basic formula as given below. It is understood that as used in this application, the term "zeolite" means and encompasses all natural and manmade forms of zeolites. All zeolites are composed of a three-dimensional framework of  $\text{SiO}_4$  and  $\text{AlO}_4$  in a tetrahedron, which creates a very high surface area. Cations and water molecules are entrained into the framework. Thus, all zeolites may be represented by the crystallographic unit cell formula:



where M represents one or more cations such as Na, K, Mg, Ca, Sr, Li or Ba for natural zeolites and  $\text{NH}_4$ ,  $\text{CH}_3\text{NH}_3$ ,  $(\text{CH}_3)_3\text{NH}$ ,  $(\text{CH}_3)_4\text{N}$ , Ga, Ge and P for manmade zeolites; n represents the cation valence; the ratio of b:a is in a range from greater than or equal to 1 and less than or equal to 5; and x represents the moles of water entrained into the zeolite framework.

**[0019]** Preferred zeolites for use in the wellbore treating fluids of the present embodiments include analcime (hydrated sodium aluminum silicate), bikitaite (lithium aluminum silicate), brewsterite (hydrated strontium barium calcium aluminum silicate), chabazite (hydrated calcium aluminum silicate), clinoptilolite (hydrated sodium aluminum silicate), faujasite (hydrated sodium potassium calcium magnesium aluminum silicate), harmotome (hydrated barium aluminum silicate), heulandite (hydrated sodium calcium aluminum silicate), laumontite (hydrated calcium aluminum silicate), mesolite (hydrated sodium calcium aluminum silicate), natrolite (hydrated sodium aluminum silicate), paulingite (hydrated potassium sodium calcium barium aluminum silicate), phillipsite (hydrated potassium sodium calcium aluminum silicate), scolecite (hydrated calcium aluminum silicate), stellerite (hydrated calcium aluminum silicate), stilbite (hydrated sodium calcium aluminum silicate) and thomsonite (hydrated sodium calcium aluminum silicate). Most preferably, the zeolites for use in the wellbore treating fluids of the present embodiment include chabazite and clinoptilolite.

**[0020]** Carrier fluids suitable for use in the embodiments of wellbore treating fluids disclosed herein comprise an aqueous fluid, such as water and water-based gels, oil-based and synthetic-based fluids, emulsions, acids, or mixtures thereof. Exemplary oil-based fluids include but are not limited to canola oil, kerosene, diesel oil, fish oil, mineral oil, sunflower oil, corn oil, soy oil, olive oil, cottonseed oil, peanut oil and paraffin. Exemplary synthetic-based fluids include but are not limited to esters, olefins and ethers.

**[0021]** The preferred carrier fluid depends upon the properties desired for the wellbore treating fluid, as well as the cost, availability, temperature, stability, viscosity, clarity, and the like, of the carrier fluid. When the carrier fluid comprises water, the water can be fresh water, unsaturated salt solution, including brines and seawater, and saturated salt solution.

**[0022]** In carrying out the methods of the present embodiments, drilling operations include drilling a wellbore with a mud, introducing a wellbore treating fluid comprising zeolite and at

least one carrier fluid into the wellbore, and forming a mass in the wellbore by allowing the wellbore treating fluid to come into contact with the mud.

[0023] Other methods according to the present embodiments include methods for performing remedial operations in a wellbore by introducing a wellbore treating fluid comprising zeolite and a carrier fluid into the wellbore, allowing the wellbore treating fluid to come into contact with a mud residing in at least one space in the wellbore such as a fissure, fracture, cavern, vug, thief zone, low pressure or high pressure subterranean zone, whereby the wellbore treating fluid forms a mass and seals the space.

[0024] The following examples are illustrative of the foregoing methods and compositions.

#### **EXAMPLE 1**

[0025] Three water-based muds, (Muds 1, 2, and 3), one oil-based mud, (Mud 4) and one synthetic-based mud (Mud 5), were obtained from Baroid Industrial Drilling Products. Muds 1 – 5 were obtained from Baroid already prepared, however the components of each mud, and the amount of each, are identified in Table 1A.

[0026] The precise chemical identification of the ester in Mud 5 obtained from Baroid is not known. However, the ester can generally be described as a monocarboxylic acid ester of a C<sub>2</sub> - C<sub>12</sub> monofunctional alkanol, wherein the monocarboxylic acid contains from 12 to 16 carbon atoms and is aliphatically saturated. Such esters are described in U.S. Patent No. 5,252,554, issued October 12, 1993 to Mueller et al. and assigned to Baroid Limited.

[0027] In addition, the precise chemical description of the following components identified in Table 1A is not known, however the function of each component is provided as follows: BARAZAN PLUS is a suspension agent/viscosifier that includes xanthan gum; EZ-MUD is a shale stabilizing polymer solution; INVERMUL, EZ-MUL, and EZ-MUL NTE are emulsifiers; GELTONE II and GELTONE V are viscosifiers; and DURATONE HT is a filtration control agent. The amount of each component is reported in Table 1A in "lb/bbl", which indicates pounds of component per barrel of mud.

[0028] Two oil-based pills comprising zeolite (Pills 1 and 2) were prepared by pouring the amount of canola oil and kerosene indicated in Table 1B into a measuring cylinder, sealing it and then shaking it back and forth by hand to form an oil mixture. The oil mixture was then poured

into a Waring blender and Arquad T-50™ surfactant was added in the amount reported in the table. Arquad T-50™ is a trimethyltallowammonium chloride (50% active) surfactant that is commercially available from ArmaK Industrial Chemicals Division. The zeolite, and lime where indicated, were added to the blender over a period of 30 seconds at a blender speed of 2000 rpm. Mixing was then continued until a homogenous mix was obtained, which took approximately 1 minute.

**[0029]** Two water-based pills comprising zeolite (Pills 3 and 4) were prepared by adding the zeolite, and lime where indicated, to water in a Waring blender over a period of 30 seconds at 2000 rpm. Mixing was then continued until a homogenous mix was obtained, which took approximately 1 minute.

**[0030]** The amounts of zeolite, canola oil, kerosene and water (as applicable) used to prepare Pills 1 – 4 are reported in the table as a weight percent (“wt. %”), while the amounts of lime and surfactant (as applicable) are reported as a weight percent of the total weight of the “base components” (“wt. % base”). The zeolite, canola oil, kerosene and water are referred to in the table as “base components” merely to provide a point of reference for the amount of lime and surfactant used to prepare Pills 1 – 4. Similarly, the lime and surfactant are referred to in the table as “additives” merely to illustrate that the amount of these components is calculated based on the total weight of the zeolite, canola oil, kerosene and water. The zeolite used to prepare Pills 1 – 4 was chabazite, which is commercially available from C2C Zeolite Corporation of Calgary, Canada.

**TABLE 1A**

<b>Components (lb/bbl)</b>	<b>Mud 1 Water Based</b>	<b>Mud 2 Water Based</b>	<b>Mud 3 Water Based</b>	<b>Mud 4 Oil Based</b>	<b>Mud 5 Synthetic Based</b>
Bentonite	15	22	15	0	0
Caustic soda	0.75	0.75	0.75	0	0
BARAZAN PLUS	0.5	0	0.5	0	0
Lime	0	1.0	0	3.0	1.0
EZ-MUD	0	0	8.93	0	0
Barite	118	117	118	0	816
Water	36.5	37.7	36.5	0	0



Components (lb/bbl)	Mud 1 Water Based	Mud 2 Water Based	Mud 3 Water Based	Mud 4 Oil Based	Mud 5 Synthetic Based
Diesel	0	0	0	26.8	0
Ester	0	0	0	0	20.8
2% CaCl <sub>2</sub> Solution	0	0	0	6.7	5.2
INVERMUL	0	0	0	7	0
EZ-MUL	0	0	0	1.5	0
EZ-MUL NTE	0	0	0	0	12
GELTONE II	0	0	0	1.5	0
GELTONE V	0	0	0	0	1.0
DURATONE HT	0	0	0	0	10

**TABLE 1B**

	Pill 1 Oil Based	Pill 2 Oil Based	Pill 3 Water Based	Pill 4 Water Based
<b>Base Components (wt. %)</b>				
Zeolite (Chabazite)	46.0	37.6	48.0	37.6
Canola Oil	32.4	37.6	0	0
Kerosene	21.6	24.8	0	0
Water	0	0	52.0	62.4
<b>Additives (wt. % Base)</b>				
Hydrated Lime	0	10.8	0	10.8
Arquad T-50	0	0.48	0	0

**[0031]** Pills 1 – 4 were then blended by hand with Muds 1 – 5 to form ten sample compositions, as indicated in **Table 1C**. Prior to blending with a pill, each mud was stirred at low speed with a Series 2000, Model 50 variable speed laboratory dispersator mixer available from Premier Mill Corp. to give a uniform suspension. When the sample was prepared from an oil-based or synthetic-based mud, 100 mL of the indicated mud (i.e., Mud 4 or 5) was placed in a cylindrical plastic container and 100 mL of the indicated water based zeolite pill (i.e., Pill 3 or 4) was added. When the sample was prepared from a water-based mud, the same procedure was followed. Namely, 100 mL of the indicated mud (i.e., Mud 1, 2, or 3) was placed in a cylindrical plastic container and 100 mL of the indicated oil based zeolite pill (i.e., Pill 1 or 2) was added.

For each of the ten samples, the plastic container was sealed with a cap, and then hand shaken for from about 30 seconds to about 1 minute, by which time the sample had turned into a mass, as reported in Table 1C. The consistency of each mass was similar to the consistency of the masses formed by conventional pills, which is often referred to as “rubbery”, “viscous”, or “gelatinous”.

**TABLE 1C**

<b>Sample No. and Blend Composition</b>	<b>Result</b>
Sample 1: Pill 1 + Mud 1	mass
Sample 2: Pill 1 + Mud 2	mass
Sample 3: Pill 1 + Mud 3	mass
Sample 4: Pill 2 + Mud 1	mass
Sample 5: Pill 2 + Mud 2	mass
Sample 6: Pill 2 + Mud 3	mass
Sample 7: Pill 3 + Mud 4	mass
Sample 8: Pill 3 + Mud 5	mass
Sample 9: Pill 4 + Mud 4	mass
Sample 10: Pill 4 + Mud 5	mass

[0032] The results of Table 1C illustrate that remedial compositions comprising zeolite, such as Pills 1 – 4, are suitable for use in any methods in which a conventional remedial composition is used to form a mass. For example, the present embodiments can be used in drilling operations and remedial operations in wellbores where a mass is formed for purposes such as sealing fissures, fractures, caverns, vugs, thief zones, low pressure subterranean zones and high pressure subterranean zones. Further still, Table 1C illustrates that remedial compositions comprising zeolite, such as Pills 1 – 4, can be either water-based or oil-based, and can be used with conventional water-based or oil-based muds.

[0033] As reported in Table 1B, Pills 2 and 4 included hydrated lime. To determine whether the hydrated lime added strength to the mass, compressive strength measurements were taken for each sample that included either Pill 2 or Pill 4, namely, Samples 4 – 6 and 9 – 10. The compressive strengths of Samples 4 – 6 and 9 – 10 were determined by placing the sealed plastic containers used to gather the data reported in Table 1C in a water bath at 180°F and atmospheric

pressure for the time periods reported in Table 1D. The plastic containers were then removed from the water bath, allowed to cool and the cylindrical samples were demolded from each plastic container. The top end of each cylindrical sample was cut using a tile saw to give a smooth and level surface. The remainder of the sample was then placed in a Tineus Olsen universal testing machine and the compressive strength determined according to operating procedures for the universal testing machine. The compressive strength measurements are reported in Table 1D.

**TABLE 1D**

Sample No.	Compressive strength (psi) Measured at 180 °F and at Time (Days)			
	5 days	10 days	15 days	20 days
Sample 4	0	0	25	25
Sample 5	0	0	25	25
Sample 6	0	0	15	15
Sample 9	27.1	26.8	not taken	not taken
Sample 10	212	164	not taken	not taken

**[0034]** The compressive strength data indicates that wellbore treating fluids comprising zeolite and an activator, such as the remedial compositions of Pills 2 and 4, form masses that develop compressive strength. Such remedial compositions are suitable for use in methods of performing drilling operations and performing remedial operations. In the embodiments illustrated by Pills 2 and 4, the activator comprised lime (also known as “calcium hydroxide”). According to other embodiments, the activator is any of sodium silicate, sodium fluoride, sodium silicofluoride, magnesium silicofluoride, zinc silicofluoride, sodium carbonate, potassium carbonate, sodium hydroxide, potassium hydroxide, sodium sulfate, and mixtures thereof.

**[0035]** In practicing methods of the present embodiments, a remedial composition comprising zeolite, such as Pills 1 – 4, is introduced into a wellbore and allowed to come into contact with a mud residing in a space such as a fissure, fracture, cavern, vug, thief zone, low pressure subterranean zone or high pressure subterranean zone in the wellbore. When the remedial composition contacts the mud, a mass forms, thereby sealing the space and preventing problems such as lost circulation. Moreover, the sealing of such spaces strengthens the wellbore

formation such that higher density muds, drilling fluids, and other wellbore treating fluids can be pumped through the wellbore without compromising the stability of the wellbore.

**[0036]** While the embodiments described herein relate to wellbore treating fluids provided as remedial compositions such as pills, it is understood that any wellbore treating fluids such as drilling, completion and stimulation fluids including, but not limited to, drilling muds, cement compositions, well cleanup fluids, workover fluids, spacer fluids, gravel pack fluids, acidizing fluids, fracturing fluids, conformance fluids, spotting fluids and the like can be prepared using zeolite and a carrier fluid. Accordingly, improved methods of the present invention comprise preparing a wellbore treating fluid using at least one carrier fluid and zeolite, as previously described herein, and placing the fluid in a subterranean formation. Other methods according to the present embodiments include performing drilling operations, completing and/or stimulating a subterranean formation, and performing primary cementing operations using a wellbore treating fluid comprising zeolite and at least one carrier fluid.

**[0037]** Other embodiments of the current invention will be apparent to those skilled in the art from a consideration of this specification or practice of the embodiments disclosed herein. However, the foregoing specification is considered merely exemplary of the present invention, with the true scope and spirit of the invention being indicated by the following claims.